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Intramolecular Charge Transfer of Conjugated Liquid Crystal Ferrocene Macromolecules

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Final Report

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Final Report

**Intramolecular Charge Transfer of Conjugated
Liquid Crystal Ferrocene Macromolecules
- Synthesis and Characterization -**

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Background. Our group at CIQA has been designing, synthesizing and characterizing organic as well as hybrid organic materials that consist of monomers and their related oligomers and polymers with nonlinear optical ‘push-pull’ and thermotropic properties that have given rise, along with other works, to several publications that underscore the successful and sustainable dynamic of the CIQA-AFRL/AFOSR/SOARD collaboration [1-7]. To date, acetylidene, phenyleneethynylene and arylenvinylidene series of macromolecules have been shown to exhibit strong two-photon absorption and thermotropic properties with mesophases dependent on the oligomer’s length as seen in the polycrystalline nature of dimmers, Smectic A (S_A) or C (S_C) phases of tetramers and pentamers, to the fluidic Nematic (N) phase of the heptamers and octamers. These liquid crystalline properties are of interest because polarized light emitters or light absorption devices, such as OLEDs, solar cells or wave guides, filters and Faraday isolators can be fabricated as nanometric films. The challenge consists of obtaining thermotropic materials with strong two photon absorption and very efficient intramolecular charge transfer (ICT).

As a first step, we have designed, synthesized and characterized a new series of conjugated macromolecules illustrated in Figure 1, which bear ferrocene [$(\eta^5-C_5H_5)Fe(\eta^5-C_5H_5)$] as a highly efficient electron donor material. The ferrocene group is coupled to 2,5-di(alcoxy) benzene ethynylene(s) as a π -conjugated connector (π) and benzoate or phenyl carboxylic acid as termini and electron attractor groups (A) to create a push-pull effect with efficient intramolecular charge transfer ($D \rightarrow \pi \rightarrow A$). The rigid, rod-like phenyleneethynylene bears flexible dodecanoxy chains which can impart liquid crystal properties. This series of materials incrementally increases the distance between the electron withdrawing and the electron donor groups, making it possible to study the relationship between, for example, the change of electric dipole moment in charge transfer transitions of these oligomers studied by ultrafast two-photon absorption and intermolecular distance.

Here, we report the synthesis and characterization of the oligomers that are presently being studied at AFRL (T. Cooper, et al.), Montana State University (A. Rebane, et al.) and CIQA by linear absorption and emission spectroscopy, laser flash photolysis, ultrafast laser femtosecond time-resolved absorption spectra and Z-scan experiments for two photon cross section measurements. Results of the spectroscopic studies will appear in subsequent reports.

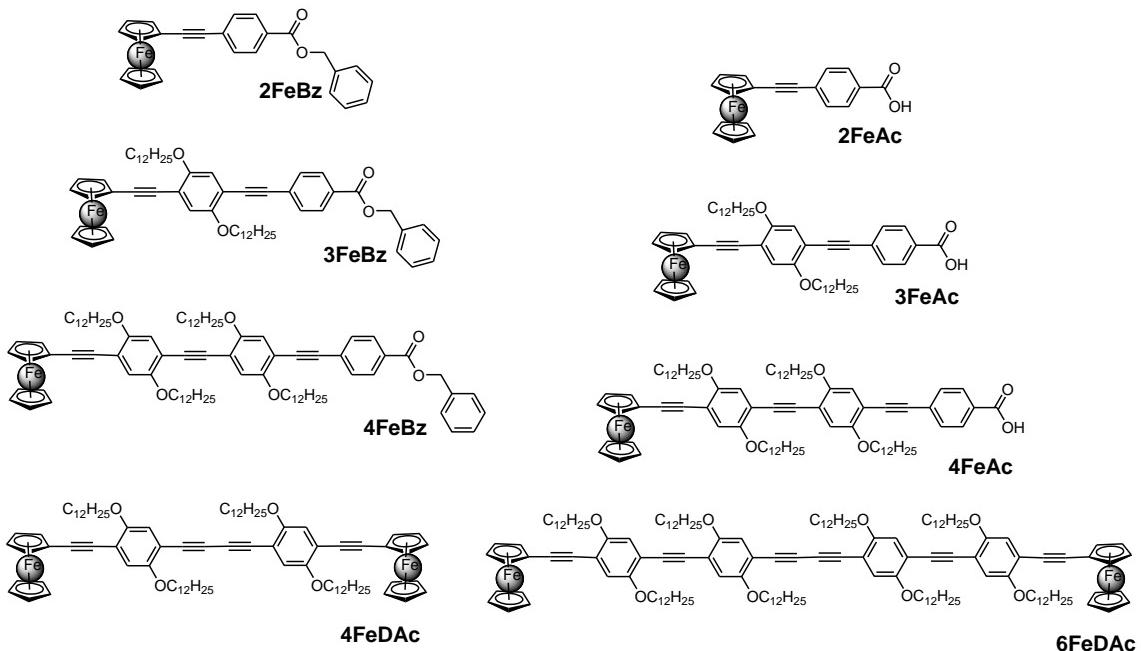


Figure 1. Molecular structure of the symmetrical and unsymmetrical ferrocenyl-ethynylene oligomers synthesized and characterized in this work.

Experimental.

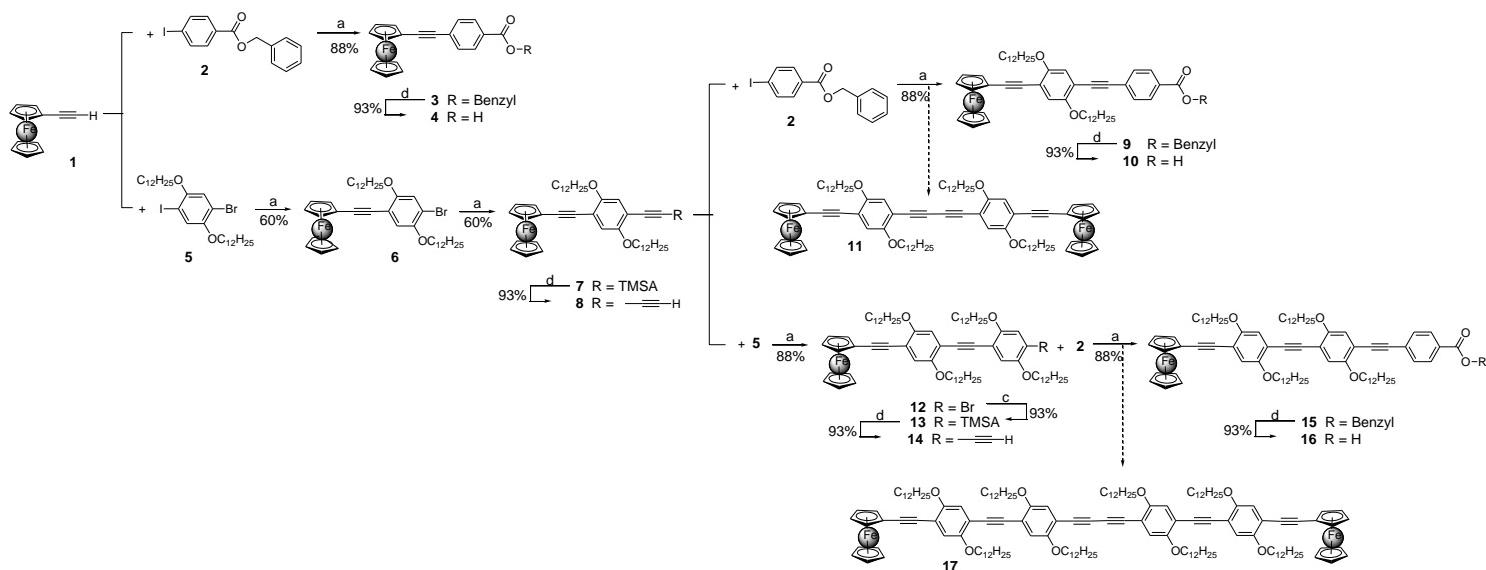
Materials. The following chemical reagents: ethynylferrocene, cuprous iodide, bis(triphenyl phosphine) palladium (II) dichloride, tetrabutylammonium fluoride (TBAF, 1M in THF), trimethylsilylacetylene (TMSA), were purchased from Aldrich and used without further purification. CHCl₃, CH₂Cl₂ and hexanes were purchased from J.T. Backer. Triethylamine (Et₃N) (Aldrich) was distilled from KOH, THF (Aldrich) was also first distilled from KOH and then from sodium benzophenone until the typical blue complex was formed. All solvents used for optical characterization were spectroscopic grade from Aldrich.

Equipment. ¹H and ¹³C NMR data were obtained at room temperature with a Jeol Eclipse spectrometer at 300 MHz for ¹H and 75.4 MHz for ¹³C using CDCl₃ as solvent and internal reference. Differential scanning calorimetry (DSC) analyses were carried out on a DuPont 951 instrument under nitrogen at a heating rate of 10 °C/min. Small and wide angle X ray scattering patterns were obtained with a Anton Paar SAXSess mc² SWAXS instrument using CuKα radiation at a wavelength of 0.1542 nm. Fluorescence lifetimes were obtained using the Time Correlated Single Photon Counting technique (TCSPC) with a TemPro (Horiba Scientific) instrument.

A nanoLED laser at 295 nm was used for the excitation; the probe measurement was obtained with a 0.01% ultrapure water suspension of LUDOX (Aldrich). Calibration of the equipment was realized with a POPOP [1,4-bis(4-methyl-5-fenil-2-oxazolyl)benzene] methanol solution (optical density <0.1 and lifetime of 0.93ns). Data were fit with the DAS6 software available with the equipment.

Synthesis.

The synthesis of the materials is illustrated in Scheme 1; yields, m.p. and solution state NMR data follow the synthesis details.



Scheme 1. Reagents and conditions: (a) $[(C_6H_5)_3P]_2PdCl_2$ (2.5 mol %), CuI (1.5 mol %), Et₃N, THF, 0 °C to r.t.; (b) KOH, toluene, N₂, 110°C, 2h; (c) $[(C_6H_5)_3P]_2PdCl_2$ (2.5 mol %), CuI (3.0 mol %), Et₃N, THF, 80 °C; (d) $^+F^+NBu_4$, THF, rt.

General procedure for the Sonogashira-Heck crosscoupling of an acetylene with a bromo- or iodoaryl. To a two neck round bottomed flask containing $[(C_6H_5)_3P]_2PdCl_2$, CuI and the bromoaryl, under nitrogen previously degassed triethylamine (and ~5 % of THF in the Godt's procedure for iodoaryls) is added via cannula. The mixture is heated at 40-45 °C for 15 min (by the Godt's method for iodoaryls, it is then cooled to ~0 °C). Then, the acetylene monomer is added (in degassed Et₃N, by the Godt's procedure in degassed THF) under nitrogen atmosphere and stirred vigorously overnight at 70-80 °C (by the Godt's method after adding the acetylene, the reaction is left to reach the room

temperature and stirred for 48 h). The mixture is filtered off to eliminate the ammonium salt, washed with THF and later the solvent evaporated. The crude product is ready for the next purification step.

General procedure for the desilylation. A round bottomed flask charged with the (trimethylsilyl)ethynyl compound, THF, two drops of water, and TBAF (0.2 equivalents per silyl group, 1M solution in THF) is stirred at room temperature for 30 minutes and then the reaction is stopped by passing it through a plug of silica gel. After the THF evaporation, the product is dried in vacuum for two hours and then used without further purification.

General procedure for the hydrolysis of the (benzyl) benzoate group. To a round bottomed flask containing, the (benzyl)benzoate terminated oligomer (1 eq.) and pulverized KOH (20 eq. per carboxylic acid), under nitrogen is added anhydrous toluene via cannula. After degassing the reactive mixture by bubbling nitrogen into the solution for 25 min, the reaction is refluxed for 90 min under nitrogen atmosphere pressure (using a rubber balloon). After cooling to room temperature, 1M HCl solution is added up to reach a pH of 2, and a precipitate formation is observed. Then, the solution is filtered, washed with toluene and H₂O and the precipitated is used without more purification. The un-hydrolyzed (benzyl) benzoate terminated oligomer is recuperated by evaporating the toluene.

Compound 2FeBz (3). Applying the general procedure for the Sonogashira cross-coupling reaction (Godt's method): To a two neck flask containing 65 mg (0.09 mmol) of [(C₆H₅)₃P]₂PdCl₂, 6 mg (0.027 mmol) of CuI and 690 mg (2.04 mmol) of **2** under nitrogen, 70 mL of degassed Et₃N were added. The mixture was heated at 45°C for 15 min and then cooled to 0°C. Later, 390 mg (1.85 mmol) of ethynylferrocene **1** dissolved in dried and nitrogen bubbled THF (3 mL) were added via syringe. The mixture was left to react to r.t. for 48 h, then the ammonium salt was filtered off and the solvent evaporated, the crude product was purified by chromatography (SiO₂, CH₂Cl₂, rf = 0.7, CH₂Cl₂:Hexanes 1:1 rf = 0.4) to obtain a deep red dust in 80 % yield. mp 128-131°C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.02 (d, 2H, Ar-H), 7.54 (d, 2H, Ar-H), 7.41 (m, 5H, Bz), 5.37 (s, 2H, -CH₂-), 4.52 (t, 2H, ArFe), 4.27 (t, 2H, ArFe), 4.25 (s, 5H, ArFe). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 166.03 (C=O), 135.99 (Ar-C), 131.19 (Ar-CH), 129.62 (Ar-CH), 128.92 (Ar-C), 128.76 (Ar-C), 128.63 (Ar-CH), 128.31 (Ar-CH), 128.24 (Ar-CH), 92.20 (-C≡C-), 85.27 (-C≡C-), 71.60 (ArFe-CH), 70.05 (ArFe-CH), 69.18 (ArFe-

CH), 66.82 (-CH₂-Ar), 64.45 (ArFe-C). UV-Vis (THF): λ_{abs} (nm) (ϵ , M⁻¹ cm⁻¹) = 273 (21,200), 311 (20,500), 365 (4,000), 448 (1,300).

Compound 2FeAc (4). Applying the general procedure for the hydrolysis of the (benzyl) benzoate group: In a 100 mL flask, 200 mg (0.48 mmol) of **3** and 535 mg (9.54 mmol) of dry and pulverized KOH were dissolved in 15 mL of dry toluene. The mixture was bubbled with nitrogen for 30 min, and refluxed for 90 min keeping a nitrogen pressure by using a rubber balloon. After cooling to room temperature, an 1M HCl water solution was added, up to obtain a precipitate that was filtered off and washed with toluene H₂O to obtain a pale orange powder in 82 % yield. mp 210-220°C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.59 (d, 2H, Ar-H), 7.10 (d, 2H, Ar-H), 4.12 (bs, 2H, ArFe), 3.89 (bs, 2H, ArFe), 3.84 (bs, 5H, ArFe). UV-Vis (THF): λ_{abs} (nm) (ϵ , M⁻¹ cm⁻¹) = 271 (16,400), 310 (15,400), 361 (3,000), 448 (920).

Compound 6. Applying the general procedure for the Sonogashira cross-coupling reaction (Godt's method): To a two neck flask containing 67 mg (0.096 mmol) of [(C₆H₅)₃P]₂PdCl₂, 6 mg (0.029 mmol) of CuI, 1.36 mg (2.094 mmol) of **5** under nitrogen, 70 mL of degassed Et₃N were added. The mixture was heated at 45°C for 15 min and then cooled at 0°C. Later, 400 mg (1.90 mmol) of ethynylferrocene **1** in THF (3 mL) was added. The mixture was left to react at r.t. for 48 h, then filtered and the salts washed with THF. After the solvents evaporation, the crude product was purified by chromatography (SiO₂, CHCl₃: hexanes 1:2, rf = 0.5) to obtain a deep red powder in 60% yield. mp 64-66°C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.08 (s, 1H, Ar-H), 6.97 (s, 1H, Ar-H), 4.42 (t, 2H, ArFe), 4.17 (m, 7H, ArFe), 3.97 (bt, 4H, -CH₂- α -O), 1.82 (m, 4H, -CH₂- β -O), 1.48 (m, 4H, -CH₂- γ -O), 1.26 (bs, 32H, -CH₂-), 0.87 (t, 6H, -CH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.24 (Ar-C-O), 149.60 (Ar-C-O), 118.10 (Ar-CH), 117.85 (Ar-CH), 113.48 (Ar-C), 112.63 (Ar-C), 93.09 (-C≡C-), 81.54 (-C≡C-), 71.56 (ArFe-CH), 70.28 (-CH₂- α -O), 70.17 (ArFe-CH), 69.94 (-CH₂- α -O), 69.36 (ArFe-CH), 65.43 (ArFe-C), 32.07, 29.83, 29.78, 29.73, 29.71, 29.56, 29.50, 29.37 (-CH₂-), 26.20 (-CH₂- γ -O), 26.13 (-CH₂- γ -O), 22.83 (-CH₂-), 14.26 (-CH₃).

Compound 7. Applying the general procedure for the Sonogashira cross-coupling reaction: To a two neck flask containing 48 mg (0.068 mmol) of [(C₆H₅)₃P]₂PdCl₂, 4 mg (0.020 mmol) of CuI, 1000-mg (1.36 mmol) of **6** under nitrogen, 100 mL of degassed Et₃N

were added. The mixture was heated at 45°C for 15 min and then, 0.267g (0.38 mL, 2.73 mmol) of TMSA was added via syringe. The mixture was left to react overnight at 60 °C. After filtering the ammonium salt and the solvent evaporation, the crude product was purified by silica gel by chromatography (SiO₂, CH₂Cl₂: hexanes, 1:3, *rf* = 0.3) to obtain a deep red powder in 78 % yield. mp 68-70°C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.91 (s, 1H, Ar-H), 6.90 (s, 1H, Ar-H), 4.49 (t, 2H, ArFe), 4.24 (s, 5H, ArFe), 4.23 (t, 2H, ArFe), 3.96 (2t, 4H, -CH₂-α-O), 1.81 (m, 4H, -CH₂-β-O), 1.51 (m, 4H, -CH₂-γ-O), 1.25 (bs, 32H, -CH₂-), 0.87 (t, 6H, -CH₃), 0.26 (s, 9H, -SiCH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.23 (Ar-C-O), 153.36 (Ar-C-O), 117.24 (Ar-CH), 116.97 (Ar-CH), 114.99 (Ar-C), 113.02 (Ar-C), 101.36 (-C≡C-), 99.67 (-C≡C-), 93.93 (-C≡C), 81.95 (-C≡C-), 71.45 (ArFe-CH), 70.03 (ArFe-CH), 69.55 (-CH₂-α-O), 69.53 (-CH₂-α-O), 68.87 (ArFe-CH), 65.30 (ArFe-C), 31.92, 29.68, 29.65, 29.46, 29.43, 29.42, 29.40, 29.36 (-CH₂-), 26.09 (-CH₂-γ-O), 26.05 (-CH₂-γ-O), 22.69, 22.55 (-CH₂-), 14.11 (-CH₃), 0.22 (-SiCH₃).

Compound 8. Applying the procedure for the desilylation: To a balloon containing 400 mg (0.53 mmol) of **7**, 20 mL of THF and two drops of water were added. Later, 0.5 mL of TBAF (1M solution in THF) was added and stirred for 30 min. Then, the mixture was passed through a plug of silica gel using THF as eluent. After the solvent evaporation, the product was dried in vacuum for 2 hours to obtain a deep red powder in 97 % yielding. mp 66-69°C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.94 (s, 1H, Ar-H), 6.93 (s, 1H, Ar-H), 4.50 (t, 2H, ArFe), 4.26 (s, 5H, ArFe), 4.24 (t, 2H, ArFe), 3.98 (2t, 4H, -CH₂-α-O), 3.33 (s, 1H, -C≡CH), 1.83 (m, 4H, -CH₂-β-O), 1.50 (m, 4H, -CH₂-γ-O), 1.26 (bs, 32H, -CH₂-), 0.87 (t, 6H, -CH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.24 (Ar-C-O), 153.36 (Ar-C-O), 117.81 (Ar-CH), 116.98 (Ar-CH), 115.46 (Ar-C), 111.90 (Ar-C), 94.06 (-C≡C), 81.95 (-C≡C-), 81.82 (-C≡C-), 80.21 (-C≡CH), 71.47 (ArFe-CH), 70.05 (ArFe-CH), 69.71 (-CH₂-α-O), 69.61 (-CH₂-α-O) 68.90 (ArFe-CH), 65.24 (ArFe-C), 31.92, 29.67, 29.65, 29.59, 29.58, 29.44, 29.43, 29.36, 29.21 (-CH₂-), 26.09 (-CH₂-γ-O), 25.94 (-CH₂-γ-O), 22.69 (-CH₂-), 14.11 (-CH₃).

Compound 9. Applying the general procedure for the Sonogashira cross-coupling reaction (Godt's method): To a two neck flask containing 22 mg (0.032 mmol) of [(C₆H₅)₃P]₂PdCl₂, 2 mg (0.0096 mmol) of CuI, 642 mg (1.90 mmol) of **2** under nitrogen, 60 mL of degassed Et₃N were added. The mixture was heated at 45°C for 15 min and then cooled at 0°C. Later, 430 mg (0.634 mmol) of **8** in THF (5 mL) were added. The mixture

was left to react at r.t. for 48 h, then filtered and the salts washed with THF. After the solvent evaporation, the crude product was purified first by precipitation in methanol, then by silica gel chromatography (CH_2Cl_2 : hexanes, 1:1, $rf = 0.6$) and finally passed through a preparative gel permeation chromatography column (Biorad, Bio-Beads SX1, toluene) to afford, after the solvent evaporation a red powder in 68 % yield. mp 49-54°C. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.05 (d, 2H, Ar-H), 7.57 (d, 2H, Ar-H), 7.41 (m, 5H, Bz), 6.99 (s, 1H, Ar-H), 6.97 (s, 1H, Ar-H), 5.37 (s, 2H, - CH_2 -), 4.51 (t, 2H, ArFe), 4.26 (s, 5H, ArFe), 4.25 (t, 2H, ArFe), 4.02 (2t, 4H, - CH_2 - α -O), 1.85 (m, 4H, - CH_2 - β -O), 1.53 (m, 4H, - CH_2 - γ -O), 1.25 (bs, 32H, - CH_2 -), 0.87 (t, 6H, - CH_3). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 165.93 (C=O), 153.88 (Ar-C-O), 153.47 (Ar-C-O), 135.93 (Ar-C), 131.40 (Ar-CH), 129.63 (Ar-CH), 129.28 (Ar-C), 128.64 (Ar-CH), 128.44 (Ar-C), 128.33 (Ar-CH), 128.25 (Ar-CH), 116.86 (Ar-CH), 115.40 (Ar-C), 112.47 (Ar-C), 94.40 (-C≡C-), 93.76 (-C≡C-), 89.39 (-C≡C-), 81.94 (-C≡C-), 71.49 (ArFe-CH), 70.07 (ArFe-CH), 69.60 (- CH_2 - α -O), 69.56 (- CH_2 - α -O), 68.95 (ArFe-CH), 66.87 (- CH_2 -Ar), 65.20 (ArFe-C), 31.93, 31.92, 29.68, 29.66, 29.64, 29.62, 29.45, 29.42, 29.37, 29.35 (- CH_2 -), 26.11 (- CH_2 - γ -O), 26.08 (- CH_2 - γ -O), 22.70 (- CH_2 -), 14.14 (- CH_3). UV-Vis (THF): λ_{abs} (nm) (ϵ , M^{-1} cm^{-1}) = 306 (28,800), 318 (28,700), 373 (31,800).

Compound 10. Applying the general procedure for the hydrolysis of the (benzyl) benzoate group: 300 mg (0.332 mmol) of **9** and 373 mg (6.64 mmol) of pulverized KOH in 20 mL of dry toluene were refluxed for 2 h. After cooling to room temperature, 1M HCl solution was added up to obtain a precipitate that was filtered off and washed with toluene and H_2O , to obtain a pale orange powder in 79 % yield. mp 133-137°C. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.08 (d, 2H, Ar-H), 7.60 (d, 2H, Ar-H), 7.0 (s, 1H, Ar-H), 6.93 (s, 1H, Ar-H), 4.52 (t, 2H, ArFe), 4.26 (s, 7H, ArFe), 4.03 (t, 4H, - CH_2 - α -O), 1.86 (m, 4H, - CH_2 - β -O), 1.55 (m, 4H, - CH_2 - γ -O), 1.25 (bs, 32H, - CH_2 -), 0.87 (t, 6H, - CH_3). UV-Vis (THF): λ_{abs} (nm) (ϵ , M^{-1} cm^{-1}) = 305 (24,500), 316 (25,300), 371 (26,900). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 153.94 (Ar-C-O), 153.46 (Ar-C-O), 131.50 (Ar-CH), 130.17 (Ar-CH), 129.29 (Ar-C), 116.87 (Ar-CH), 116.83 (Ar-CH), 115.52 (Ar-C), 112.36 (Ar-C), 94.48 (-C≡C-), 93.66 (-C≡C-), 89.89 (-C≡C-), 81.92 (-C≡C-), 71.50 (ArFe-CH), 70.07 (ArFe-CH), 69.60 (- CH_2 - α -O), 69.56 (- CH_2 - α -O), 68.96 (ArFe-CH), 65.17 (ArFe-C), 31.94, 31.93, 29.71, 29.70, 29.69, 29.67, 29.46, 29.43, 29.38, 29.36 (- CH_2 -), 26.12 (- CH_2 - γ -O), 26.11 (- CH_2 - γ -O), 22.71 (- CH_2 -), 14.14 (- CH_3). UV-Vis (THF): λ_{abs} (nm) (ϵ , M^{-1} cm^{-1}) = 306 (28,800), 318 (28,700), 373 (31,800).

Compound 11. Applying the general procedure for the Sonogashira cross-coupling reaction: To a two-neck round-bottomed flask containing 5.0 mg (7.4×10^{-3} mmol) of $[(C_6H_5)_3P]_2PdCl_2$, 1mg (4.4×10^{-3} mmol) of CuI (3.0 % mol) and 100 mg (0.147 mmol) of **8** , Et₃N/THF 49:2.5 (v/v). The reaction was heated to 70 °C and stirred under nitrogen for 16 h. After filtering the ammonium salt and the solvent evaporated, the crude product was first precipitated in methanol, purified by column chromatography (SiO₂, hexanes: CH₂Cl₂, 1:1, rf=0.4) and then by preparative gel permeation chromatography column (Biorad, Bio-Beads SX1, toluene) to afford, after solvent evaporation, a pale orange powder in 92 % yield. mp. 99-101 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.98 (s, 2H, Ar-H), 6.95 (s, 2H, Ar-H), 4.53 (bs, 4H, ArFe), 4.27 (s, 14H, ArFe), 4.01 (2t, 8H, -CH₂-α-O), 1.86 (m, 8H, -CH₂-β-O), 1.54 (m, 8H, -CH₂-γ-O), 1.28 (bs, 64H, -CH₂-), 0.90 (t, 12H, -CH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 155.03 (Ar-C-O), 153.34 (Ar-C-O), 117.59 (Ar-CH), 116.90 (Ar-CH), 115.80 (Ar-C), 111.83 (Ar-C), 94.76 (-C≡C-), 81.96 (-C≡C-), 79.61 (-C≡C-), 79.11 (-C≡C-), 71.50 (ArFe-CH), 70.07 (ArFe-CH), 69.80 (-CH₂-α-O), 69.51 (-CH₂-α-O), 68.97 (ArFe-CH), 65.16 (ArFe-C), 31.94, 29.72, 29.71, 29.68, 29.66, 29.46, 29.39, 29.18 (-CH₂-), 26.11 (-CH₂-γ-O), 25.96 (-CH₂-γ-O), 22.71 (-CH₂-), 14.14 (-CH₃). UV-Vis (THF): λ_{abs} (nm) (ϵ , M⁻¹ cm⁻¹) = 287 (26,500), 304 (25,800), 315 (26,000), 395 (45,700).

Compound 12. Applying the general procedure for the Sonogashira cross-coupling reaction (Godt's method): To a two-neck round-bottomed flask containing 27 mg (3.8×10^{-2} mmol) of $[(C_6H_5)_3P]_2PdCl_2$, 2 mg (1.2×10^{-3} mmol) of CuI (3.0 % mol) and 497 mg (0.764 mmol) of **5**, Et₃N/THF 49:2.5 (v/v) were added. The mixture was heated at 45°C for 15 min and then cooled to 0°C. Later, 518 mg (0.764 mmol) of **8** in THF (5 mL) were added. The mixture was left to react at r.t. for 48 h, then filtered and the salts washed with THF. After the solvent evaporation, the crude product was purified first by precipitation in methanol, then by silica gel chromatography (CH₂Cl₂: hexanes, 1:1, rf = 0.7) to afford a pale orange powder in 87 % yield. mp 53-57°C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.09 (s, 1H, Ar-H), 7.0 (s, 1H, Ar-H), 6.97 (s, 1H, Ar-H), 6.95 (s, 1H, Ar-H), 4.50 (t, 2H, ArFe), 4.25 (m, 7H, ArFe), 3.98 (bt, 8H, -CH₂-α-O), 1.82 (m, 8H, -CH₂-β-O), 1.49 (m, 8H, -CH₂-γ-O), 1.26 (bs, 64H, -CH₂-), 0.87 (t, 12H, -CH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.00 (Ar-C-O), 153.51 (Ar-C-O), 149.48 (Ar-C-O), 118.24 (Ar-CH), 117.69 (Ar-CH), 117.16 (Ar-CH), 116.96 (Ar-CH), 114.70 (Ar-C), 113.49 (Ar-C), 113.16 (Ar-C), 113.06 (Ar-C), 93.95 (-C≡C-), 90.76 (-C≡C-), 90.55 (-C≡C-), 82.03 (-C≡C-), 71.48 (ArFe-

CH), 70.07 (-CH₂-α-O), 70.05 (ArFe-CH), 69.99, 69.74, 69.49 (-CH₂-α-O), 68.89 (ArFe-CH), 65.34 (ArFe-C), 31.94, 29.68, 29.62, 29.60, 29.49, 29.48, 29.44, 29.38, 29.27, 29.23, 26.15, 26.02, 26.01, 25.95, 22.70 (-CH₂), 14.14 (-CH₃).

Compound 13. Applying the general procedure for the Sonogashira cross-coupling reaction: 10 mg (1.37 X 10⁻² mmol) of [(C₆H₅)₃P]₂PdCl₂, 1 mg (4.11 X 10⁻³ mmol) of CuI, 330-mg (1.36 mmol) of **12**, 100 mL of degassed Et₃N. The mixture was heated at 45°C for 15 min and then, 81 mg (114 μL, 0.823 mmol) of TMSA was added via syringe. The mixture was left to react overnight at 60 °C. After filtering the ammonium salt and the solvent evaporation, the crude product was purified by silica gel by chromatography (SiO₂, CH₂Cl₂: hexanes, 1:2, rf = 0.4) to obtain a red-brown powder in 83 % yield. mp 58-62°C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.90 (s, 1H, Ar-H), 6.89 (s, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 6.87 (s, 1H, Ar-H), 4.44 (t, 2H, ArFe), 4.18 (s, 5H, ArFe), 4.17 (t, 2H, ArFe), 3.93 (2t, 8H, -CH₂-α-O), 1.76 (m, 8H, -CH₂-β-O), 1.45 (m, 8H, -CH₂-γ-O), 1.18 (bs, 64H, -CH₂-), 0.81 (t, 12H, -CH₃), 0.19 (s, 9H, -SiCH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.20 (Ar-C-O), 153.53 (Ar-C-O), 153.50 (Ar-C-O), 153.30 (Ar-C-O), 117.45 (Ar-CH), 117.14 (Ar-CH), 116.97 (Ar-CH), 114.71 (Ar-C), 114.68 (Ar-C), 113.57 (Ar-C), 113.52 (Ar-C), 101.24 (-C≡C-), 100.03 (-C≡C-), 93.97 (-C≡C-), 91.70 (-C≡C-), 91.12 (-C≡C-), 82.05 (-C≡C-), 71.47 (ArFe-CH), 70.06 (ArFe-CH), 69.74, 69.69, 69.46, 69.42 (-CH₂-α-O), 68.89 (ArFe-CH), 65.34 (ArFe-C), 31.94, 29.69, 29.66, 29.50, 29.47, 29.42, 29.39, 29.36, 29.33, 26.16, 26.10, 26.02, 25.99, 22.71 (-CH₂), 14.15 (-CH₃), -0.01 (-SiCH₃).

Compound 14. Applying the procedure for the desilylation: 175 mg (0.144 mmol) of **13**, 10 mL of THF, two drops of water and 0.3 mL of TBAF (1M solution in THF). The mixture was stirred for 30 min, then passed through a plug of silica gel using THF as eluent. The product was dried in vacuum for 2 hours to obtain a deep red powder in 98 % yielding. mp 54-62 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.92 (s, 1H, Ar-H), 6.91 (s, 1H, Ar-H), 6.90 (s, 1H, Ar-H), 6.89 (s, 1H, Ar-H), 4.44 (t, 2H, ArFe), 4.19 (s, 5H, ArFe), 4.17 (t, 2H, ArFe), 3.93 (2t, 8H, -CH₂-α-O), 3.26 (s, 1H, -C≡CH), 1.76 (m, 8H, -CH₂-β-O), 1.42 (m, 8H, -CH₂-γ-O), 1.28 (bs, 64H, -CH₂), 0.81 (t, 12H, -CH₃).

¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.16 (Ar-C-O), 153.56 (Ar-C-O), 153.50 (Ar-C-O), 153.26 (Ar-C-O), 117.99 (Ar-CH), 117.12 (Ar-CH), 116.98 (Ar-CH), 116.97 (Ar-CH), 115.08 (Ar-C), 114.78 (Ar-C), 113.42 (Ar-C), 112.43 (Ar-C), 94.01 (-C≡C-), 91.75 (-

C≡C-), 90.89 (-C≡C-), 82.23 (-C≡CH-), 82.03 (-C≡C-), 80.09 (-C≡CH), 71.46 (ArFe-CH), 70.05 (ArFe-CH), 69.75, 69.73, 69.58, 69.47 (-CH₂-α-O), 68.89 (ArFe-CH), 65.32 (ArFe-C), 31.94, 29.69, 29.63, 29.61, 29.48, 29.39, 29.30, 29.20, 26.15, 26.01, 25.97, 22.71 (-CH₂-), 14.14 (-CH₃).

Compound 15. Applying the general procedure for the Sonogashira cross-coupling reaction (Godt's method): 7 mg (1.1 X 10⁻² mmol) of [(C₆H₅)₃P]₂PdCl₂, 1 mg (3.1 X 10⁻³ mmol) of CuI, 212-mg (0.63 mmol) of **2**, 50 mL of degassed Et₃N. The mixture was heated at 45°C for 15 min and then, 245 mg (0.209 mmol) of **14** was added via syringe. The mixture was left to react at r.t. for 48 h, then filtered and the salts washed with THF. The crude product was first precipitated in methanol, purified by column chromatography (SiO₂, hexanes: CH₂Cl₂, 1:1, rf=0.4) and then by preparative gel permeation chromatography column (Biorad, Bio-Beads SX1, toluene) to afford, after solvent evaporation, a pale orange powder in 71 % yield. mp 54-58°C. ¹H δ (ppm) 8.05 (d, 2H, Ar-H), 7.58 (d, 2H, Ar-H), 7.42 (m, 5H, Bz), 7.02 (s, 1H, Ar-H), 7.01 (s, 1H, Ar-H), 6.98 (s, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 5.38 (s, 2H, -CH₂-), 4.51 (t, 2H, ArFe), 4.26 (s, 5H, ArFe), 4.25 (t, 2H, ArFe), 4.02 (2t, 8H, -CH₂-α-O), 1.85 (m, 8H, -CH₂-β-O), 1.52 (m, 8H, -CH₂-γ-O), 1.24 (bs, 64H, -CH₂-), 0.87 (bt, 12H, -CH₃). UV-Vis (THF): λ_{abs} (nm) (ϵ , M⁻¹ cm⁻¹) = 318 (34,500), 398 (49,500). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 165.91 (C=O), 153.85 (Ar-C-O), 153.57 (Ar-C-O), 153.51 (Ar-C-O), 153.43 (Ar-C-O), 135.93 (Ar-C), 131.43 (Ar-CH), 129.64 (Ar-CH), 129.33 (Ar-C), 128.64 (Ar-CH), 128.39 (Ar-C), 128.33 (Ar-CH), 128.25 (Ar-CH), 117.13 (Ar-CH), 116.98 (Ar-CH), 116.95 (Ar-CH), 115.11 (Ar-C), 114.81 (Ar-C), 113.44 (Ar-C), 113.10 (Ar-C), 94.05 (-C≡C-), 94.01 (-C≡C-), 92.06 (-C≡C-), 91.07 (-C≡C-), 89.29 (-C≡C-), 82.05 (-C≡C-), 71.47 (ArFe-CH), 70.06 (ArFe-CH), 69.76 (-CH₂-α-O), 69.74 (-CH₂-α-O), 69.51 (-CH₂-α-O), 69.48 (-CH₂-α-O), 68.90 (ArFe-CH), 66.88 (-CH₂-Ar), 65.33 (ArFe-C), 31.94, 29.72, 29.65, 29.50, 29.48, 29.45, 29.39, 29.36, 29.33, 26.16, 26.11, 26.03, 26.00, 22.71 (-CH₂-), 14.15 (-CH₃).

Compound 16. Applying the general procedure for the hydrolysis of the (benzyl) benzoate group: 260 mg (0.191 mmol) of **15** and 198 mg (3.82 mmol) of pulverized KOH in 20 mL of dry toluene were refluxed for 2 h. After cooling, 1M HCl solution was added up to obtain a precipitate that was filtered off and washed with toluene and H₂O, to obtain a pale orange powder in 79 % yield. mp 94-97 °C. ¹H δ (ppm) 8.09 (d, 2H, Ar-H), 7.61 (d, 2H, Ar-H), 7.02 (s, 1H, Ar-H), 7.01 (s, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.96 (s, 1H, Ar-

H), 4.51 (t, 2H, ArFe), 4.26 (s, 5H, ArFe), 4.25 (t, 2H, ArFe), 4.03 (2t, 8H, -CH₂-α-O), 1.86 (m, 8H, -CH₂-β-O), 1.52 (m, 8H, -CH₂-γ-O), 1.25 (bs, 64H, -CH₂-), 0.87 (bt, 12H, -CH₃). UV-Vis (THF): λ_{abs} (nm) (ϵ , M⁻¹ cm⁻¹) = 316 (34,600), 395 (49,400). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 153.60 (Ar-C-O), 153.50 (Ar-C-O), 153.41 (Ar-C-O), 131.53 (Ar-CH), 130.90 (Ar-CH), 130.14 (Ar-CH), 129.19 (Ar-C), 128.81 (Ar-CH), 117.12 (Ar-CH), 117.01 (Ar-CH), 115.26 (Ar-C), 114.82 (Ar-C), 114.60 (Ar-C), 113.41 (Ar-C), 113.04 (Ar-C), 94.06 (-C≡C-), 93.94 (-C≡C-), 92.13 (-C≡C-), 91.05 (-C≡C-), 89.81 (-C≡C-), 82.04 (-C≡C-), 71.47 (ArFe-CH), 70.06 (ArFe-CH), 69.75 (-CH₂-α-O), 69.54 (-CH₂-α-O), 69.48 (-CH₂-α-O), 68.90 (ArFe-CH), 65.33 (ArFe-C), 31.94, 29.71, 29.67, 29.51, 29.49, 29.40, 29.37, 29.34, 26.16, 26.14, 26.07, 26.03, 26.02, 22.71 (-CH₂-), 14.15 (-CH₃).

Compound 17. Applying the general procedure for the Sonogashira cross-coupling reaction: To a two-neck round-bottomed flask containing 7.0 mg (8.7 X 10⁻³ mmol) of [(C₆H₅)₃P]₂PdCl₂, 1mg (5.22 X 10⁻³ mmol) of CuI (3.0 % mol) and 200 mg (0.174 mmol) of **16**, Et₃N/THF 49:3.0 (v/v). The reaction was heated to 70 °C and stirred under nitrogen for 16 h. After filtering the ammonium salt and the solvent evaporated, the crude product was first precipitated in methanol, purified by column chromatography (SiO₂, hexanes: CH₂Cl₂, 1:1, rf=0.3) and then by preparative gel permeation chromatography column (Biorad, Bio-Beads SX1, toluene) to afford a pale orange powder in 93 % yield. mp. 90-93°C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.99 (bs, 8H, Ar-H), 4.53 (bs, 4H, ArFe), 4.27 (bs, 14H, ArFe), 4.03 (bs, 16H, -CH₂-α-O), 1.86 (bs, 16H, -CH₂-β-O), 1.52 (bs, 16H, -CH₂-γ-O), 1.27 (bs, 128H, -CH₂-), 0.89 (bs, 24H, -CH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 155.00 (Ar-C-O), 153.59 (Ar-C-O), 153.51 (Ar-C-O), 153.30 (Ar-C-O), 117.89 (Ar-CH), 117.13 (Ar-CH), 117.02 (Ar-CH), 117.00 (Ar-CH), 115.53 (Ar-C), 114.86 (Ar-C), 113.41 (Ar-C), 112.47 (Ar-C), 94.08 (-C≡C-), 92.38 (-C≡C-), 91.07 (-C≡C-), 82.06 (-C≡C-), 79.63 (-C≡C-), 79.35 (-C≡C-), 71.47 (ArFe-CH), 70.05 (ArFe-CH), 69.73 (-CH₂-α-O), 69.49 (-CH₂-α-O), 68.91 (ArFe-CH), 65.34 (ArFe-C), 31.94, 29.73, 29.48, 29.39, 29.36, 29.30, 29.19, 26.16, 26.00, 22.71 (-CH₂-), 14.14 (-CH₃). UV-Vis (THF): λ_{abs} (nm) (ϵ , M⁻¹ cm⁻¹) = 310 (41,400), 397 (61,600), 409 (61,900).

Results of linear absorption and emission spectroscopy, laser flash photolysis, ultrafast laser femtosecond time-resolved absorption spectra and Z-scan experiments for two photon cross section measurements will appear in subsequent reports.

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